Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. This research was also supported in part by the National Resource for Computation in Chemistry under a grant from the National Science Foundation (Grant CHE-7721305) and the Basic Energy Sciences Division of the U.S. Department of Energy (Contract No. W-7405-ENG-48). Mr. P. Cheeseman kindly provided the program to create the stereoplots.

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Formation of Stable Bilayer Assemblies in Dilute Aqueous Solution from Ammonium Amphiphiles with the Diphenylazomethine Segment

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Abstract: Quaternary ammonium amphiphiles of the following structures were synthesized: C_n-BB-N^+3C_1 and C_n-BB-C_m-N^+3C_1, where C_n and C_m are hydrocarbon chains of $n = 0, 4, 7, 12$ and $m = 4, 10$, and BB and N^+3C_1 denote 4,4′-diphenylazomethine moiety and trimethylammonium group, respectively. These amphiphiles gave clear or slightly turbid solutions when dispersed in water by the sonication or injection method. The aqueous solutions contained extraordinarily large aggregates: 10^6–10^7 daltons except for BB-N^+3C_1 and C_4-BB-N^+3C_1, as estimated by the light scattering method. The critical micelle concentration was 10^{-4}–10^{-5} M when the hydrocarbon tail (C_n portion) was present. Electron microscopy indicated that these aggregates ($n = 7$ and 10) possessed lamellar or vesicle structures which were composed of the bilayer assembly (layer thickness 40–60 Å). The bilayer structure could not be detected for amphiphiles of $n = 0$ and 4. The C_m portion did not appear to affect the aggregate structure. NMR spectroscopy and differential scanning calorimetry suggested the liquid crystalline property of these aqueous aggregates. In conclusion, the stable bilayer assembly similar to that of biomembranes was prepared in dilute aqueous solution from single-chain ammonium amphiphiles which possessed a rigid segment.

The major components of the lipid bilayer of biomembranes are phospholipids which possess two long alkyl chains. The reason why these biolipids produce at low concentrations the bilayer structure instead of globular micelles has been frequently discussed.[1,2] Among various structural features the existence of the two alkyl chains was shown to be essential for the bilayer formation by recent developments in these laboratories that stable bilayer assemblies were readily formed from a variety of synthetic dialkyl amphiphiles of C_{10}–C_{18}. The hydrophilic group of these amphiphiles may be cationic (ammonium and sulfonium),[3-5] anionic (sulfonate, phosphate, and carboxylate),[6] nonionic (polyoxyethylene),[7] or zwitterionic.[7] Similar studies were reported by other workers.[8-10]

On the other hand, we suspected that the liquid-crystalline nature of bilayers (both natural and synthetic) is the cause and not the result of the bilayer formation. Then it should be possible to find bilayer-forming amphiphiles whose structures are quite different from those of dialkyl amphiphiles. Diphenylazomethine derivatives belong to a major class of liquid-crystalline materials.[11] Therefore, we prepared a series of ammonium amphiphiles which possess the diphenylazomethine moiety and studied their aggregation behavior in *dilute*

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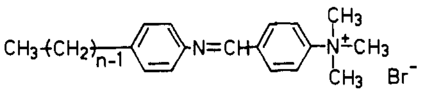
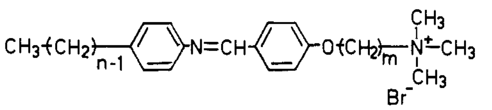
aqueous solution. The amphiphile structures are shown below together with abbreviations.



C_n-BB-N^+3C_1 n = 0, 4, 7, 12



C_n-BB-C_m-N^+3C_1 (n = 0, 4, 7, 12; m = 4, 10)

Experimental Section

Amphiphiles C_n-BB-N^+3C_1 and C_n-BB-C_m-N^+3C_1 were prepared by condensation of *p*-alkylanilines and para-substituted benzaldehydes.

(*p*-Formylphenyl)trimethylammonium Bromide. *p*-Formyl-*N*,*N*-dimethylaniline was allowed to react with excess methyl bromide in benzene in a sealed ampule at 100 °C for 70 h. The precipitates were collected and washed with benzene: pale yellow needles; yield 60–80%; mp 208–210 °C; NMR δ (D_2O) 3.8 (s, 9 H, N^+CH_3), 8.2 (s, 4 H, phenyl), 10.0 (s, 1 H, CHO).

4-(*p*-Formylphenyloxy)butyltrimethylammonium Bromide. According to the procedure of Donahoe et al.,[12] 2.3 g (0.1 mol) of sodium metal was dissolved in 200 mL of absolute ethanol, and then 64.8 g (0.30 mol) of 1,4-dibromobutane and 12.4 g (0.10 mol) of *p*-hydroxybenzaldehyde were added at once. After refluxing for 4 h, the reaction mixture was poured into 500 mL of ice water and the oily product was extracted with chloroform. The organic layer was dried over Na_2SO_4, solvent removed in vacuo, and the residue distilled: colorless oil; yield 15 g (58%); bp 145–147 °C (0.01 mm). *p*-(4-Bromobutyloxy)benzaldehyde thus obtained (15 g, 0.06 mol) was dissolved in 80 mL of ethanol and allowed to react with 106 g (0.6 mol) of 30% aqueous trimethylamine in a sealed ampule at 100 °C for 38 h. Solvent was then removed in vacuo and the precipitates were recrystallized from ethanol: colorless needles; yield 16 g (86%); mp 201 °C; NMR δ (Me_2SO-d_6) 3.1 (s, 9 H, N^+CH_3), 7.2 (d) and 7.9 (d, 4 H, phenyl), 10.0 (s, 1 H, CHO).

10-(*p*-Formylphenyloxy)decyltrimethylammonium Bromide, *p*-(10-Bromodecanoxyl)benzaldehyde was similarly obtained in 64% yield from 1,10-dibromodecane and *p*-hydroxybenzaldehyde: colorless oil, bp 185–195 °C (0.01 mm). Subsequent reaction with trimethylamine produced the corresponding ammonium bromide: colorless needles; yield 74%; mp 117–118 °C; NMR δ (Me_2SO-d_6) 3.1 (s, 9 H, N^+CH_3), 7.2 (d) and 7.9 (d, 4 H, phenyl), 10.0 (s, 1 H, CHO).

Diphenylazomethine Amphiphiles. These ammonium salts were subsequently condensed with equimolar *p*-alkylanilines (Kanto Kagaku Co.) in refluxing ethanol for 30 min in the presence of small amounts of acetic acid. After cooling to room temperature, precipitates were collected and recrystallized two to four times from ethanol, yields 50–80%. NMR and IR spectra were consistent with the expected structures. Liquid crystalline textures were observed for the series of C_n-BB-C_m-N^+3C_1 (m = 4 and 10) during the melting point measurement by a polarizing microscope. These temperature ranges were indicated by the arrow. BB-N^+-$3C_1$: mp 187 °C. Anal. ($C_{16}H_{19}N_2Br$) C, H, N. C_4-BB-N^+3C_1: mp 180 °C. Anal. ($C_{20}H_{27}N_2Br \cdot H_2O$) H, N; C: calcd, 64.00; found, 63.45. C_7-BB-N^+3C_1: mp 165–166 °C. Anal. ($C_{23}H_{33}N_2Br$) C, H, N. C_{12}-BB-N^+3C_1: mp 152–153 °C. Anal. ($C_{28}H_{43}N_2Br \cdot H_2O$) C, H, N. C_4-BB-C_4-N^+3C_1: mp 145 → 190 °C. Anal. ($C_{24}H_{35}N_2OBr \cdot {}^1\!/_2H_2O$) H, N; C: calcd, 63.31; found, 62.82. C_7-BB-C_4-N^+3C_1: mp 115 → 145 °C. Anal. ($C_{27}H_{41}N_2OBr$) N; C: calcd, 66.26; found, 67.76. H: calcd, 8.38; found, 8.85. C_{12}-BB-C_4-N^+3C_1: mp 80 → 120 °C. Anal. ($C_{32}H_{55}N_2OBr \cdot H_2O$) C, H, N. BB-$C_{10}N^+3C_1$: mp 190 → 210 °C. Anal. ($C_{26}H_{39}N_2OBr$) C, H, N. C_4-BB-C_{10}-N^+3C_1: mp 170 → 190 °C. Anal. ($C_{30}H_{47}N_2OBr \cdot {}^1\!/_2H_2O$) C, H, N. C_7-BB-C_{10}-N^+3C_1: mp 165 → 195 °C. Anal. ($C_{33}H_{53}N_2OBr$) C, H, N. C_{12}-BB-C_{10}-N^+3C_1: mp 97 → 128 °C. Anal. ($C_{38}H_{63}N_2OBr$) N; C: calcd, 70.92; found, 73.89. H: calcd, 9.80; found, 10.40.

Table I. Aggregate Structure of Single-Chain Amphiphiles

amphiphile	cmc, mM	aggregate weight, daltons[a]	electron micrograph[b]
BB-N^+3C_1	>10	$<10^4$	no structure
C_4-BB-N^+3C_1	0.22	1×10^5	no structure
C_7-BB-N^+3C_1	0.06	8×10^6	lamella
C_{12}-BB-N^+3C_1	0.01	4×10^6	vesicle and lamella
C_4-BB-C_4-N^+3C_1	0.16	8×10^6	no structure
C_7-BB-C_4-N^+3C_1	0.01	2×10^7	lamella
C_{12}-BB-C_4-N^+3C_1	0.01	4×10^6	vesicle
BB-C_{10}-N^+3C_1	>10	4×10^6	no structure
C_4-BB-C_{10}-N^+3C_1	0.33	6×10^6	no structure
C_7-BB-C_{10}-N^+3C_1	0.02	2×10^7	vesicle
C_{12}-BB-C_{10}-N^+3C_1	0.01	1×10^7	lamella

[a] Aggregate weights were estimated by light scattering at a fixed angle of 90°. [b] Sample solutions were prepared by the injection procedure.

Electron Microscopy. The sample solution was prepared either by the sonication method (A) or by the injection method (B). In method A, 4–5 mg of an amphiphile was suspended in 1 mL of deionized water and sonicated for 2–5 min using a Branson sonifier, Model 185 (sonic power 40). Slightly turbid solutions were thus obtained. In method B, 10 mg of an amphiphilic compound was dissolved in 1 mL of appropriate water-soluble solvents (ethanol for C_n-BB-N^+3C_1 and C_n-BB-C_4-N^+3C_1 and DMF for C_n-BB-C_{10}-N^+3C_1), and 100 μL of the solution was slowly injected by using a microsyringe into 1 mL of warm water (50–60 °C) and sonicated for 2–5 min. Clear solutions were obtained.

One milliliter of these sample solutions (10 mM or ca. 0.5 wt %) was mixed with 1 mL of 2% aqueous uranyl acetate, sonicated for ca. 20 s. The mixture was incubated in ice-water for 30 min and applied to carbon-coated grids which were then dried in vacuo. A Hitachi electron microscope, Model H-500, was used for the measurement.

Light-Scattering Experiment. Slightly turbid or translucent solutions of the amphiphiles were prepared by the sonication method and filtered through a 1-μ Sartorius filter (Type MF 4). Light scattering was measured at a fixed angle of 90° using a laser light source (Union Giken Co., Japan, Model LS-600), light source He-Ne laser (632.8 nm). The scattering intensity at other angles was less reproducible. Therefore, the data at 90° for solutions of 2.5, 5.0, and 10.0 mM (0.125, 0.25, and 0.50 wt %, respectively) were extrapolated to zero concentration, and the extrapolated data was used to estimate the aggregate weight. Although the angle dependence of the scattering intensity was neglected, the aggregate weight should have at least the order-of-magnitude reliability.

Surface Tension. The surface tension was measured by the Wilhelmy method (Digi-O-matic instrument, Model ESB-IV (Kyowa Kagaku Co., Japan)). DMF solutions of the amphiphiles were added in portions to water at room temperature and the surface tension was measured each time. The maximal amount of added DMF was 3 v/v %, which did not affect the surface tension of pure water.

Differential Scanning Calorimetry. Sixty microliters each of aqueous solutions of the amphiphiles (1.5 wt %) was sealed in a silver sample pan. The measurements were made with a differential scanning calorimeter SSC-560 (Daini Seikosha Co., Ltd., Japan): heating rate, 1.2 °C/min; 0.025 mcal s^{-1} full scale^{-1}; chart speed, 0.5 cm/min.

Results and Discussion

Aggregation Behavior. Some of the aggregation behavior of the amphiphiles is summarized in Table I. The critical micelle (aggregate) concentration was inferred from inflections of plots of amphiphile concentration and surface tension.

It is seen that these amphiphiles start to aggregate at 10^{-4}–10^{-5} M except for BB-N^+-$3C_1$ and BB-C_{10}-N^+3C_1, which did not show appreciable lowering of surface tension. The minimal surface tension was 20–30 dyn cm^{-1}.

The cmc is lowered by lengthening of the hydrocarbon tail (C_n portion), but is affected little by the length of the intervening methylene group (C_m portion). Thus the cmc's of C_4-BB-N^+-$3C_1$, C_4-BB-C_4-N^+3C_1, and C_4-BB-C_{10}-N^+3C_1

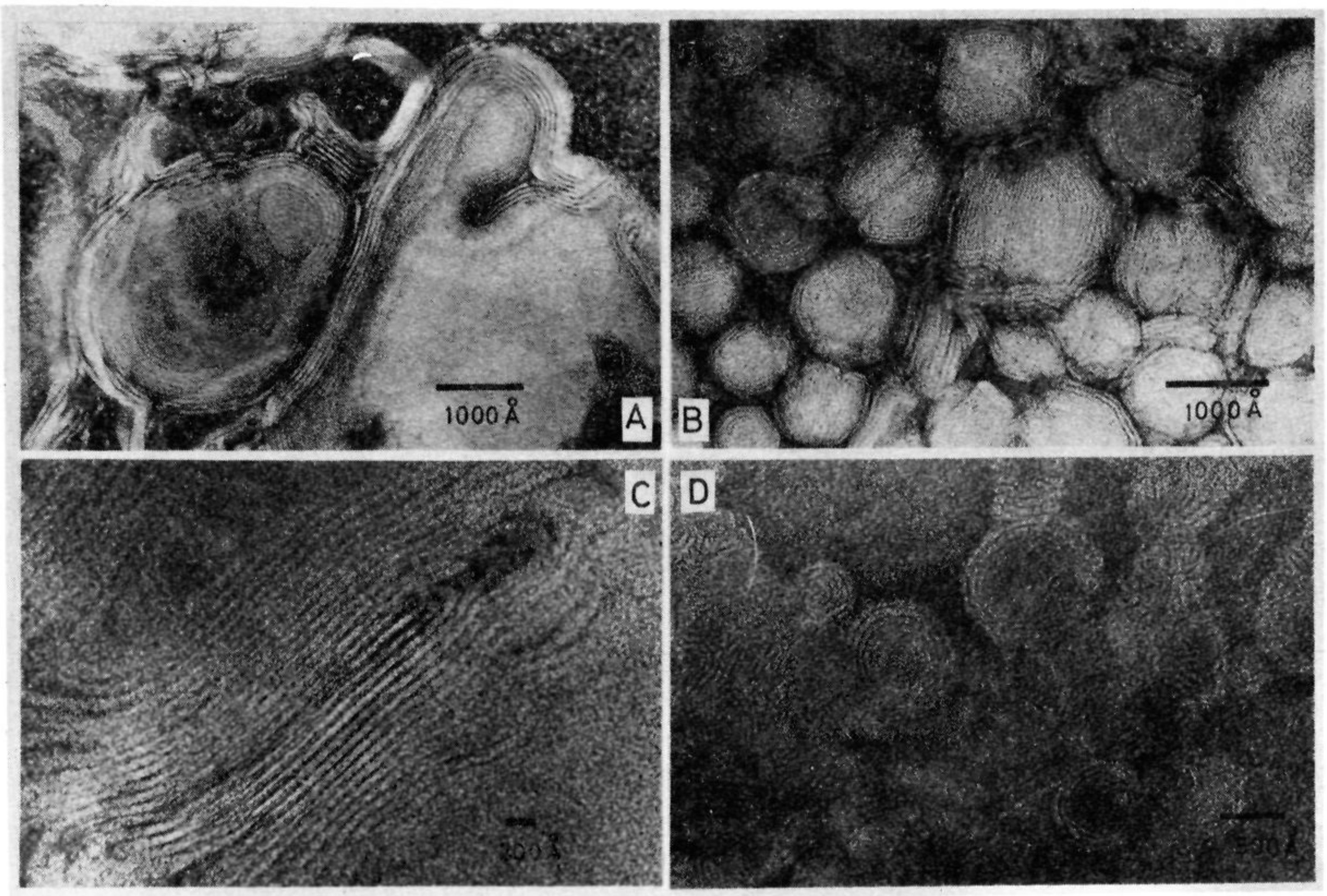


Figure 1. Electron micrographs. Sample solution, 10 mM. A: C_{12}-BB-N^+3C_1, magnification ×100 000. B: C_{12}-BB-C_4-N^+3C_1, magnification ×120 000. C: C_{12}-BB-$C_{10}N^+3C_1$, magnification ×180 000. D: C_7-BB-C_{10}-N^+3C_1, magnification ×150 000.

lie in the range of (2–3) × 10^{-4} M. It is interesting that the aggregation behavior of BB-C_{10}-N^+3C_1 shows a remarkable contrast with that of C_{12}-BB-N^+3C_1 or of C_7-BB-C_4-N^+3C_1. In terms of the hydrophilic–lipophilic balance the former and latter compounds should show similar aggregation behavior. That it is not so implies that the location of the rigid segment determines to a large degree the tendency of these amphiphiles to align at the water–air interface.

The average molecular weight of most of the aggregates was 10^6–10^7. Therefore, the average aggregation numbers are in the range of 10^3–10^5. These values are much larger than those of the conventional globular micelle: the aggregation number is usually 50–100 for common ammonium surfactants.[13] It is interesting that the aggregate weight for BB-C_{10}-N^+3C_1 is very large (4 × 10^6 daltons) in spite of its lack of surfactant activity in the surface-tension measurement.

Morphology of Aggregates. The morphologies of these aggregates as inferred from electron micrographs are given in Table I. The dispersion procedure (sonication or injection) did not alter the aggregate structure. Layer structures were observed for all the amphiphiles which possess hydrocarbon tails of C_7 and C_{12}. When the hydrocarbon tail is butyl or nonexistent, structure formation could not be detected. Some of the electron micrographs are shown in Figure 1. Electron micrographs for the series of C_{12}-BB-C_m-N^+3C_1 (m = 0, 4, 10) show the presence of lamellar and/or filled vesicle structures (Figures 1A–C). The layer thickness is 40–60 Å and seemingly increases with increasing lengths of the C_m chain. The observed layer thickness is consistent with the formation of the bilayer membrane structure, as is the case for phospholipids and synthetic dialkyl amphiphiles; see Figure 2. Dark streaks running through the middle of each layer may be caused by deposition of uranyl acetate, as suggested by Kajiyama et al.[14] When the hydrocarbon tail is C_7, the layer structure is somewhat less developed. Filled (multilayered) vesicles are clearly seen in an electron micrograph of the aggregate of C_7-BB-C_{10}-N^+3C_1 (Figure 1D). On the other hand, partially developed lamellar structures (fingerprint-like) were observed for C_7-BB-C_4-N^+3C_1 and C_7-BB-N^+3C_1.

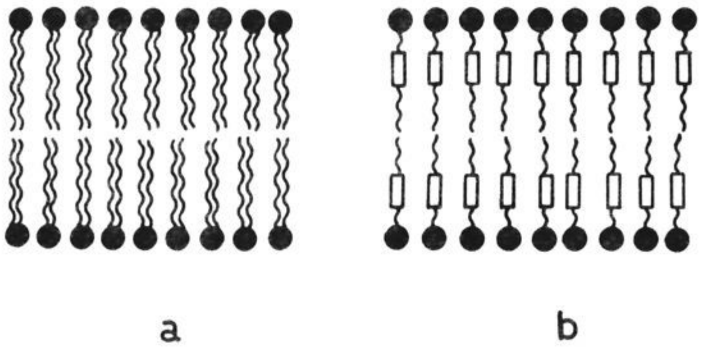


Figure 2. Schematic illustrations of synthetic bilayer membranes. Filled circle, hydrophilic head group; wavy line, flexible hydrocarbon chain; rectangle, rigid segment. (a) double-chain amphiphile; (b) single-chain amphiphile.

These electron microscopic observations establish the structural requirement for single-chain amphiphiles in the formation of the stable bilayer in dilute aqueous solution: the single-chain amphiphile must possess both a rigid molecular segment and a flexible hydrocarbon tail. The development of the bilayer structure is improved with increasing chain length of the flexible tail (C_n portion), the minimal chain length lying probably between C_7 and C_4. It is worthy of emphasis that BB-C_{10}-N^+3C_1 and C_4-BB-C_{10}-N^+3C_1 fail to form well-organized aggregates in spite of their formation of very large aggregates as inferred from the light scattering experiment. As mentioned above, the bilayer structure develops only when the flexible hydrocarbon moiety is present as a tail. The length of the C_m chain does not affect the morphology to detectable degrees. The rigid segment may be the diphenylazomethine moiety as shown in the present study or the biphenyl group.[15] It appears that most of the rigid molecular fragment included in thermotropic liquid crystalline molecules can be used for this purpose. In the absence of the rigid segment, single-chain ammonium amphiphiles form fluid globular micelles in dilute

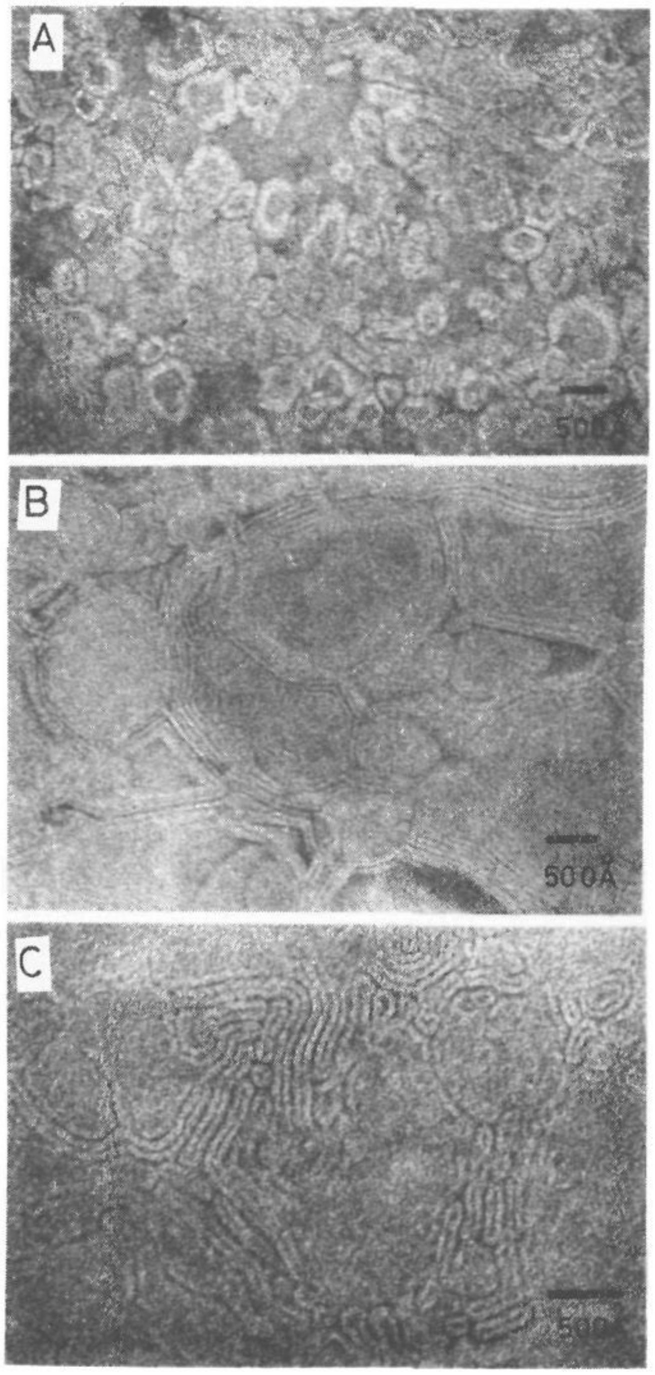
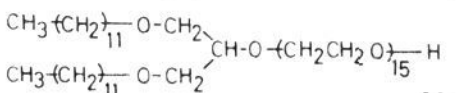


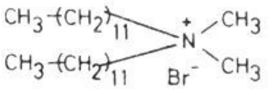
Figure 3. Electron micrographs. Sample solution, 10 mM. A: C_{12}-BB-$N^{+}3C_{1}$ + C_{12}-BB-C_{10}-$N^{+}3C_{1}$ (equimolar mixture), magnification ×90 000. B: C_{12}-BB-$N^{+}3C_{1}$ + cholesterol (3:1 molar mixture), magnification ×100 000. C: C_{12}-BB-$N^{+}3C_{1}$ + $2C_{12}$-Gly-15G (equimolar mixture), magnification ×150 000.

aqueous solution: lyotropic mesophases may be formed in soap–water systems only at very high concentrations (26 wt % in the case of CTAB).[16,17]

The aggregate morphology may be modified by addition of second components. Figure 3 shows examples of the morphological modification. When an equimolar mixture of C_{12}-BB-$N^{+}3C_{1}$ and C_{12}-BB-C_{10}-$N^{+}3C_{1}$ was dispersed in water, a clear solution was obtained and single-walled vesicles were observed conspicuously (Figure 3A). A similar observation was made for a slightly turbid solution of an equimolar mixture of C_{12}-BB-C_{4}-$N^{+}3C_{1}$ and C_{12}-BB-C_{10}-$N^{+}3C_{1}$. It appears that single-walled vesicles are predominantly formed instead of the lamellar structure, when two amphiphiles in which the location of the rigid segment is different are mixed. Addition of 30 mol % of cholesterol to a 10 mM solution of C_{12}-BB-$N^{+}3C_{1}$ gave rise to an electron micrograph shown in Figure 3B. The lamellar structure can be seen. Equimolar mixtures of C_{12}-BB-$N^{+}3C_{1}$ with $2C_{12}$-gly-15G and with $2C_{12}N^{+}2C_{1}$ produced single-walled vesicles (Figure 3C) and multiwalled vesicles, respectively. The latter dialkyl compounds form vesicles by themselves in dilute aqueous solution.[3,7] Monoalkyl surfactants destroy the bilayer structure; e.g., an equimolar mixture of C_{12}-BB-C_{m}-$N^{+}3C_{1}$ (m = 0, 4, 10) and CTAB did not give a well-organized structure.



$2C_{12}$-gly-15G



$2C_{12}\,N^{+}2C_{1}$

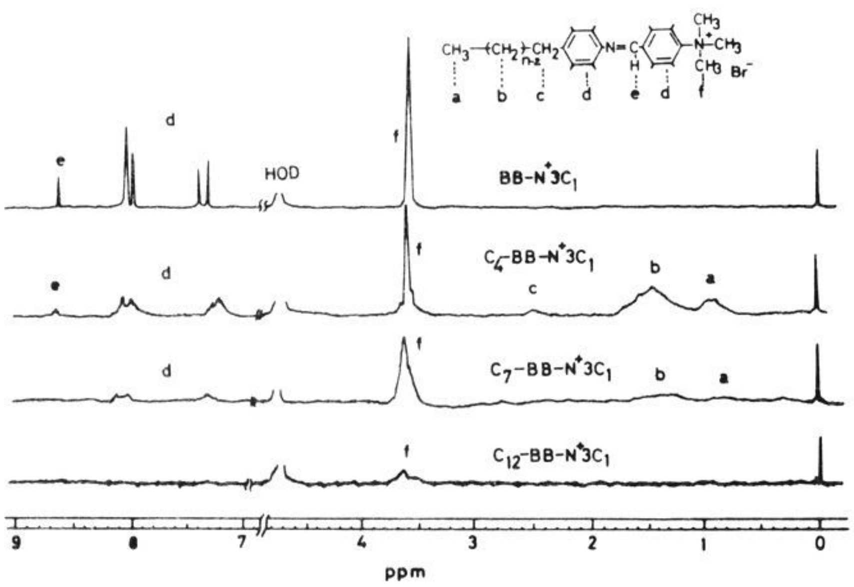


Figure 4. ^{1}H NMR spectra of C_{n}-BB-$N^{+}3C_{1}$ in D_2O, concentration 0.5 wt % (10 mM), 2000–3000 scan, internal reference DSS.

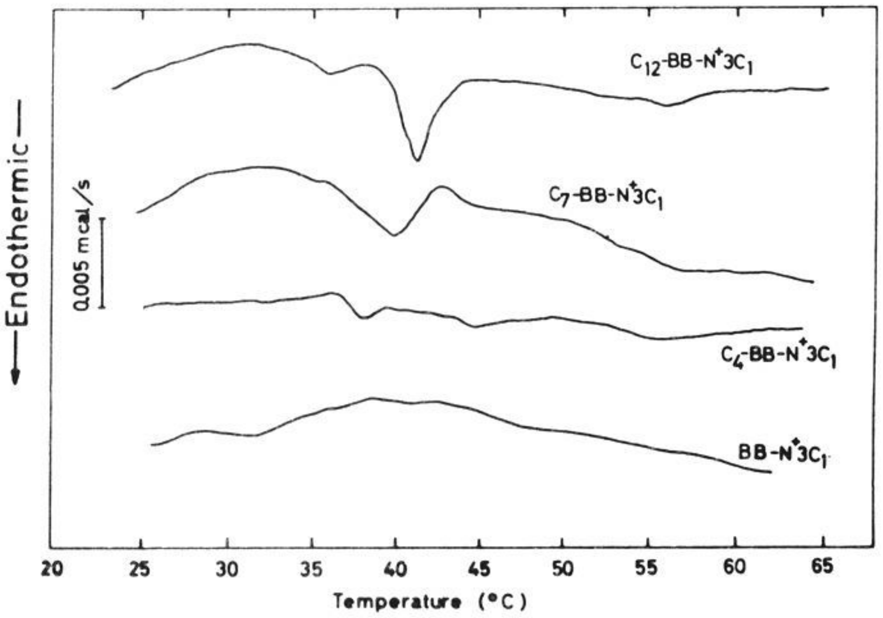


Figure 5. Differential scanning calorimetry of C_{n}-BB-$N^{+}3C_{1}$, concentration 1.5 ± 0.3 wt % in water, heating rate 1.2 °C/min.

Molecular Movement in Bilayers. Considerable broadening of ^{1}H NMR peaks has been observed in aqueous (D_2O) solution of synthetic bilayers.[3,6] Nagamura et al. investigated in detail the temperature dependence of the ^{1}H NMR spectrum of several double-chain ammonium amphiphiles, and concluded that the broadening was attributable to the restricted molecular motion as in phospholipid bilayers.[18] Figure 4 shows ^{1}H NMR spectra of 10 mM aqueous solutions of C_{n}-BB-$N^{+}3C_{1}$ (n = 0, 4, 7, and 12) at ambient temperature. Peak broadening was not detected for BB-N^{+}-$3C_{1}$, but the extent of broadening was enhanced with increasing lengths of the hydrocarbon tail. This trend is consistent with that of the bilayer formation (electron microscopy) in this series of compounds and suggests that the molecular motion is restricted when the bilayer structure is sufficiently developed.

Figure 5 is a collection of DSC (differential scanning calorimetry) curves for *dilute* aqueous solutions (1.5 wt %) of the same series of the amphiphile (C_{n}-BB-$N^{+}3C_{1}$). A clear endothermic peak is found at 40 °C for C_{12}-BB-$N^{+}3C_{1}$. This peak moves to lower temperatures as the hydrocarbon tail becomes shorter. The peak height decreases simultaneously. The phase transition between solid and liquid crystalline states has been observed for aqueous solutions of the synthetic bilayer of double-chain ammonium amphiphiles.[14,18] Therefore, this peak may also be attributed to the phase transition. The enthalpy change at the 40 °C peak of C_{12}-BB-N^+3C_1 is 0.51 kcal/mol. This figure is only ca. 6% of that reported for dipalmitoylphosphatidylcholine (7.8-8.5 kcal/mol) at its phase transition.[19,20] It is possible that the change in the molecular motion at the phase transition becomes less drastic when the dialkyl chain is replaced by the partially rigid, single chain.

Stability of Bilayer Assemblies. The azomethine group is not very stable chemically, and it is reported that liquid crystals of benzylidenaniline derivatives are readily hydrolyzed at room temperature in the presence of organic acids.[21] However, the bilayer membrane of C_{12}-BB-C_m-N^+3C_1 (m = 0, 4, 10) is hydrolytically stable in water, and identical electron micrographs were obtained after the aqueous solutions (10 mM) had been kept for more than 3 months at ambient temperature. The stability is lowered for the amphiphiles that have shorter hydrocarbon tails, and oily products began to separate 4 months after preparation of a 10 mM solution of C_4-BB-C_4-N^+3C_1. The rate of hydrolytic decomposition was determined quantitatively using λ_{max} at 280 nm of the diphenylazomethine group. The reaction is acid catalyzed and plots of log k_{obsd} (first-order rate constant of hydrolysis) vs. pH give a linear relation with slope of -1 in the range of pH 2-8. At pH 7 (Tris buffer) and 30 °C, decomposition of 1×10^{-5} M of C_{12}-BB-C_m-N^+3C_1 (m = 0, 4, and 10) and C_7-BB-C_{10}-N^+3C_1 was very slow and k_{obsd} was estimated to be not larger than 10^{-7} s^{-1} (half-life > 100 days). The hydrolysis of BB-N^+3C_1 is faster and k_{obsd} was estimated to be 10^{-3} s^{-1}. These kinetic data are consistent with the above-mentioned observation of the stability of the amphiphile solution.

Concluding Remarks. Although the black membrane (plate bilayer) can be prepared from a variety of compounds other than biolipids,[22] aqueous dispersions of the stable bilayer assembly have been produced only from phospholipids (natural dialkyl amphiphile) and synthetic dialkyl amphiphiles. There are recent articles which claims formation of the bilayer assembly from single-chain fatty acids;[23,24] however, these aggregates are not well characterized at the molecular level and not sufficiently stable. Thus, to our best knowledge, the present paper reports for the first time the formation of stable bilayer assemblies from single-chain amphiphiles as a *dilute* aqueous dispersion. It is now possible to prepare stable bilayers from a variety of synthetic single-chain and double-chain amphiphiles. Even stable monolayer membranes were formed as an extension of the present work.[25] These aqueous organizations may be used in the near future to create new molecular devices such as energy transducers, specific transport systems, chemical sensers, etc.

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